



**ESTIMATING THE CONTRIBUTION OF COAL-FIRED POWER PLANTS TO
THE ATMOSPHERIC DEPOSITION OF MERCURY
IN WISCONSIN**

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Document CP263-1a

June 2007

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EXECUTIVE SUMMARY

This report presents an estimation of the contribution of coal-fired power plants to the atmospheric deposition of mercury in Wisconsin. Modeling of the contribution of Wisconsin coal-fired power plants to atmospheric deposition of mercury in Wisconsin was conducted in 2002 using the chemical transport model TEAM. A 1999/2000 emission inventory updated with data from the Wisconsin Department of Natural Resources was used. Model performance was evaluated with available measurements and was considered satisfactory. The results of the model simulations led to the conclusion that Wisconsin coal-fired power plants contributed from 1 to 4% to mercury deposition at the four Wisconsin sites of the Mercury Deposition Network and contributed less than 5% over most areas of Wisconsin.

A review of studies conducted since 2002 was conducted to assess whether the results of the 2002 modeling are affected by new results and the extent to which these new studies show similar findings regarding mercury deposition in Wisconsin. We summarize the conclusions of these new studies below.

- Recent advances in our knowledge of atmospheric mercury processes do not have any significant effect on the results of the 2002 study.
- The statistical analysis of mercury wet deposition measurements collected in Steubenville, Ohio, led to an estimate of the contribution of coal combustion sources to mercury wet deposition at that location which is consistent with the prediction of TEAM for that same location, thereby corroborating the ability of TEAM to simulate the effect of emission reduction scenarios on mercury deposition (as was done in the 2002 study).
- Estimates of the contribution of all natural sources and anthropogenic sources outside of North America to mercury deposition in Wisconsin have been made by AER, Harvard University and the U.S. EPA using different modeling systems. Those estimates range from 60 to 85%, i.e., anthropogenic North American sources are estimated to contribute between 15 and 40% to mercury deposition in Wisconsin. (Note that the larger estimates of the North American anthropogenic source contribution are obtained with the AER modeling system, which includes TEAM; other groups estimate lower contribution from North American anthropogenic sources.)
- Calculations of mercury deposition were conducted by EPA using the CMAQ and REMSAD chemical transport models. EPA calculated with CMAQ that all U.S. coal-fired power plants contributed on average 8.4% to total mercury deposition in Wisconsin. EPA calculated with REMSAD that less than 5% of mercury emitted from Wisconsin anthropogenic sources is deposited within Wisconsin.

- New studies have shown that the TEAM results are likely to overestimate the contribution of coal-fired power plants to mercury deposition in the vicinity of those plants:
 - (1) Grid-based models such as TEAM, CMAQ and REMSAD overestimate mercury deposition in the vicinity of elevated sources such as power plants.
 - (2) Reduction of Hg^{II} to Hg^0 may occur in coal-fired power plant plumes, thereby leading to less local mercury deposition of those estimated Hg^{II} emissions.
 - (3) Large storm systems may lead to contribution to wet deposition of mercury from the upper atmosphere, which is not currently taken into account in existing models.

In summary, the results of the 2002 study of mercury deposition in Wisconsin are still valid and studies conducted since 2002 either corroborate or further validate those results.

1. Background

Atmospheric & Environmental Research, Inc. (AER) conducted in 2002 a computer model simulation of atmospheric mercury deposition to estimate the effect of various mercury emission scenarios on atmospheric mercury deposition in Wisconsin. These simulations were conducted with the Trace Element Analysis Model (TEAM), a three-dimensional model of the fate and transport of atmospheric mercury. The results of these simulations were documented in a report titled “Modeling Deposition of Atmospheric Mercury in Wisconsin” (Vijayaraghavan et al., 2002).

In this document, we provide first a brief overview of the current understanding of atmospheric mercury. Next, we describe the chemical transport model used in our simulations and we summarize here the results of the simulations pertaining to the contribution of Wisconsin coal-fired power plants to atmospheric mercury deposition in Wisconsin. Then, we present the results of recent relevant studies conducted since 2002 by AER and other organizations including the U.S. Environmental Protection Agency (EPA), Harvard University, the University of Michigan and Atmospheric Research & Analysis, Inc. (ARA). We summarize these studies and discuss whether our earlier conclusions are affected by these new results, and the extent to which these studies show similar findings regarding mercury deposition.

2. Overview of Atmospheric Mercury

Mercury is present in the atmosphere mostly as gaseous elemental mercury, Hg^0 , gaseous divalent mercury, Hg^{II} (also called reactive gaseous mercury or RGM), and particulate mercury, Hg_p . Particulate mercury in the atmosphere could arise from divalent mercury becoming adsorbed to atmospheric particulate matter after it is emitted in vapor form or from divalent mercury being emitted into the atmosphere as particulate matter directly from the source. In the global atmosphere, Hg^0 accounts on average for more than 90% of total mercury, Hg^{II} accounts for a few %, and Hg_p accounts for less than 1%. Mercury species can be converted from Hg^0 to Hg^{II} and vice-versa, as depicted in Figure 1. Most atmospheric Hg^{II} occurs as inorganic compounds (with traces of organic monomethylmercury of unknown origin), while organic Hg^{II} mostly occurs in water bodies.

Mercury is emitted from natural sources as well as from anthropogenic sources. In addition, some of the mercury from both of these types of sources that is deposited to the Earth’s surface is emitted back to the atmosphere (mostly as Hg^0). Current total (both natural and anthropogenic) emissions of mercury are estimated to be between 6000 and 7000 Mg/year (1 Mg = 1 metric ton = 1.1 ton). About two thirds of those total emissions are considered to be of anthropogenic origin (with an uncertainty range of one half to three quarters). About half of world-wide anthropogenic emissions are estimated to originate from Asia. Total U.S. anthropogenic emissions are less than 10% of the world-wide anthropogenic emissions. U.S. coal-fired power plants are estimated to contribute 44% to the anthropogenic emissions of mercury in the United States but contribute less

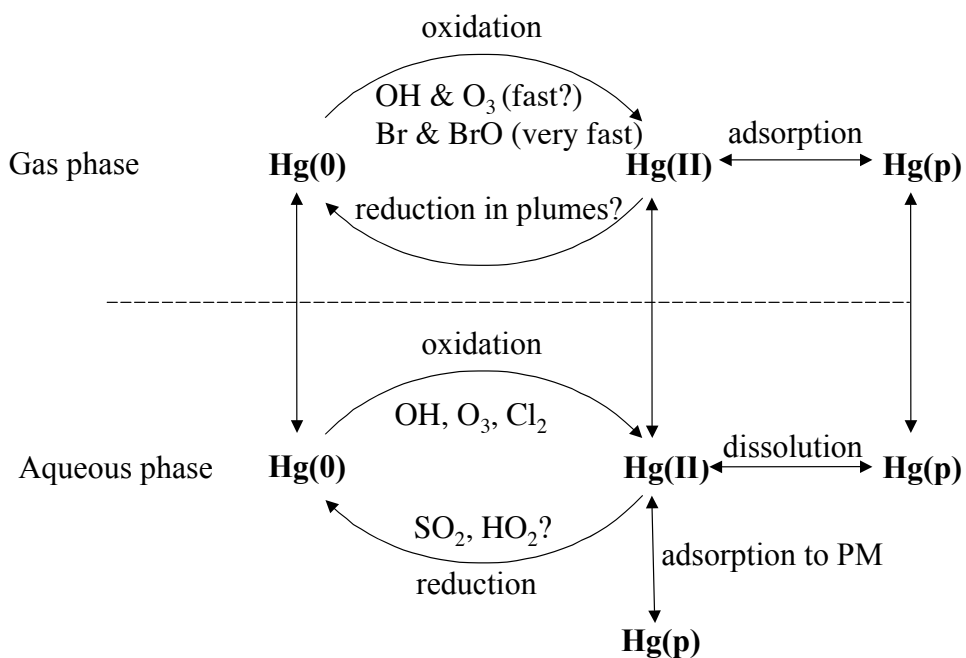


Figure 1. Schematic representation of the atmospheric chemistry of mercury (Source: Lindberg et al., 2007).

than 1% to the total world-wide emissions of mercury. Mercury emissions from Wisconsin coal-fired power plants currently constitute about 2.5% of U.S coal-fired power plant mercury emissions and less than 0.02% of total world-wide emissions of mercury.

The relative fractions of Hg^0 , Hg^{II} and Hg_p vary among the sources of mercury. Natural sources (oceans, volcanoes, mercuriferous soils) emit mostly Hg^0 . Emission of mercury from soils, water and vegetation occurs mostly as Hg^0 . Anthropogenic sources emit Hg^0 , Hg^{II} and Hg_p in different proportions depending on the source type. Waste incinerators tend to emit mostly Hg^{II} , chlor-alkali plants emit mostly Hg^0 and coal-fired power plants emit a combination of Hg^0 and Hg^{II} with proportions that depend on the type of coal burned, the type of boiler, and the type of emission control equipment.

Mercury is removed from the atmosphere via both wet deposition (precipitation) and dry deposition (interaction with surfaces) processes to the Earth's surface. Hg^0 , Hg^{II} , and Hg_p have very different deposition characteristics. The removal of Hg^0 from the atmosphere via dry and wet deposition is very slow because Hg^0 is believed to have a low dry deposition velocity and has very low solubility in water. Thus, Hg^0 tends to be transported globally. Hg^{II} species are more water soluble than Hg^0 and adsorb readily on most surfaces. However, Hg^{II} may be converted to Hg^0 before it is deposited to the Earth's surface, thus decreasing the local and regional deposition impacts of Hg^{II} emissions. Hg_p can be present in particles of various sizes. Fine particles have an atmospheric lifetime of several days in the absence of precipitation; coarse particles are removed faster than fine particles from the atmosphere. Hg_p is present in very small fractions (<2%) in coal-fired power plant emissions and hence have a minimal contribution to mercury deposition.

The atmospheric lifetime of mercury is estimated to be in the range of 0.5 to 1.5 years based on estimates of global emissions and the global pool of atmospheric mercury. It must be noted that Hg can cycle several times between the Hg^{II} and Hg^0 species before being removed from the atmosphere by deposition and, consequently, the atmospheric lifetime of the individual species is significantly less (2 to 3 months for Hg^0 and hours to days for Hg^{II}).

3. Chemical Transport Models

Chemical transport models (CTMs) are mathematical representations of the physical and chemical processes that govern the behavior of chemical species in the atmosphere. They use as inputs the emissions into the atmosphere of the chemical species of interest, the meteorology (winds, temperature, pressure, humidity, clouds and precipitation), land use (urban area, forest, water, etc.) and upwind concentrations of the chemical species of interest. Most CTMs that are applied to large domains (such as a region, a continent or the globe) use a gridded representation of the atmosphere, i.e., the atmosphere is divided into a three-dimensional mesh of contiguous volumes (grid cells). For each grid cell, the CTM calculates as a function of location and time the evolution of the concentrations of the chemical species of interest due to emissions from

anthropogenic and natural sources, transport by the winds, dispersion due to atmospheric turbulence, chemical transformations due to reactions in the gas phase, particles and droplets (clouds or fogs), and deposition to the Earth's surface by wet and dry processes. The output of a CTM includes the concentrations of the simulated chemical species in each grid cell and their deposition to the Earth's surface for each surface grid cell.

CTMs have been used for the past thirty years to simulate air quality, e.g. ozone and particulate matter (PM) concentrations, and to assist decision makers in the development of cost-effective emission control strategies. CTMs have also been used to address atmospheric deposition including, for example, acid deposition as part of the National Acid Precipitation Assessment Program (NAPAP) and mercury deposition as part of the Clean Air Mercury Rule (CAMR).

CTMs are needed to estimate the effect of future reductions or growth in emissions of air pollutants on air quality and atmospheric deposition because many air pollutants are transported over very large domains and because changes in their emissions vary in time and space and, in some cases, may not have a proportional effect on the air pollutant concentrations. For example, reductions in mercury emissions due to installation of equipment to control SO₂ and NO_x emissions from coal-fired power plants may occur along with changes in the speciation of the mercury emissions. Because the different mercury species have distinct atmospheric behaviors, and because atmospheric reactions involving SO₂ and NO_x can also impact mercury atmospheric fate and transport, the changes in mercury deposition cannot be estimated directly from the changes in total mercury emissions. Therefore, a CTM that represents the atmospheric processes governing the spatial and temporal evolution of mercury species is needed to calculate the effect of emission changes on atmospheric mercury deposition patterns.

4. The Trace Element Analysis Model (TEAM)

The model used in the 2002 study of mercury deposition in Wisconsin is the Trace Element Analysis Model (TEAM) which is a three-dimensional grid-based CTM that simulates the emissions, transport, chemical and physical transformations, and wet and dry deposition of atmospheric mercury species. The atmosphere is approximated by a three-dimensional grid mesh. Mercury species move between grid cells according to the winds and atmospheric turbulence, which are obtained from a computer simulation performed at the National Oceanic and Atmospheric Administration (NOAA). Within each grid cell, chemical transformations occur that oxidize Hg⁰ to Hg^{II} and, in the presence of clouds, reduce Hg^{II} to Hg⁰. The mercury chemical mechanism used in TEAM and the global mercury CTM used for boundary conditions has been reported by Seigneur et al. (2006a) and represents the state of the science. Changes made since 2002 are discussed in Section 6. The speciated mercury emissions inventory used in this modeling system has been described by Seigneur et al. (2004); Wisconsin-specific emissions are described in Section 5. Precipitation removes Hg^{II} and Hg_p from the atmosphere and wet deposition is calculated accordingly in TEAM.

In the lowest grid cell layer of the model (i.e., near the surface of the Earth), dry deposition of Hg^0 , Hg^{II} and Hg_p occurs and those species are removed from the atmosphere. Clouds and precipitation are obtained from actual data available from the National Center for Atmospheric Research (NCAR) and the National Atmospheric Deposition Program (NADP). The TEAM simulations presented here used 1998 meteorology. The concentrations of most species (ozone, hydroxyl radicals, sulfur dioxide, hydrogen peroxide and hydroperoxyl radicals) reacting with mercury are obtained from results of model simulations conducted at Harvard University. Other atmospheric constituents (chlorine compounds, particulate matter) involved in mercury transformations are derived from literature values. It is possible to use the values of these species reacting with mercury as an input to the model because mercury concentrations are so low that they have a negligible effect on the concentrations of the species with which mercury reacts. The concentrations of mercury species that are transported from upwind (i.e. global background) into the modeling domain (i.e., North America) are obtained from a global model simulation. The global model simulates the same processes as TEAM but uses a coarser spatial resolution to cover the entire globe. Figure 2 depicts the multi-scale (global/ continental/regional) modeling domains used in this study. The nested continental/ regional domain over North America comprises an outer domain with a horizontal grid resolution of 100 km over the United States and an inner domain with a horizontal grid resolution of about 20 km over the upper Midwest, Northeast and parts of Ontario and Quebec. Wisconsin is included in the inner domain. The vertical resolution consists of six layers from the surface to 6 km altitude with finer resolution near the surface (the layer interfaces are at 60, 150, 450, 850 and 2000 m).

TEAM calculates the concentrations of mercury species (Hg^0 , Hg^{II} and Hg_p) in every grid cell for every hour of the year and the wet and dry deposition fluxes (i.e. deposition rate per unit surface area) of these mercury species in every surface grid cell for every hour of the year. Concentrations of mercury species in the atmosphere are typically expressed in ng/m^3 for Hg^0 and pg/m^3 for Hg^{II} and Hg_p ($1 \text{ ng}/\text{m}^3 = 1$ billionth of a gram per cubic meter of air; $1 \text{ pg}/\text{m}^3 = 1$ thousandth of $1 \text{ ng}/\text{m}^3$). Deposition fluxes are typically reported for Hg^{II} and Hg_p because most Hg^0 that is dry deposited is assumed to be emitted back to the atmosphere (see discussion of emissions of mercury above). These model output values are then added for the entire year to provide dry, wet and total (i.e., dry + wet) deposition fluxes of mercury; they are expressed in $\mu\text{g}/\text{m}^2\text{-year}$.

TEAM has been used over the past ten years to simulate mercury deposition over North America and various regions of the United States. Its ability to predict mercury deposition has been evaluated against available data for mercury wet deposition that are available from the Mercury Deposition Network (MDN) and available concentrations of mercury species collected by various research groups and its performance has been found to be satisfactory (Seigneur et al., 2004). TEAM has also been used to estimate mercury deposition to the five Great Lakes. Mercury deposition over the Great Lakes simulated with TEAM is comparable to that estimated by Landis and Keeler (2002) in the Lake Michigan Mass Balance Study in 1994-95 and other Great Lake studies (Vijayaraghavan et al., 2005).

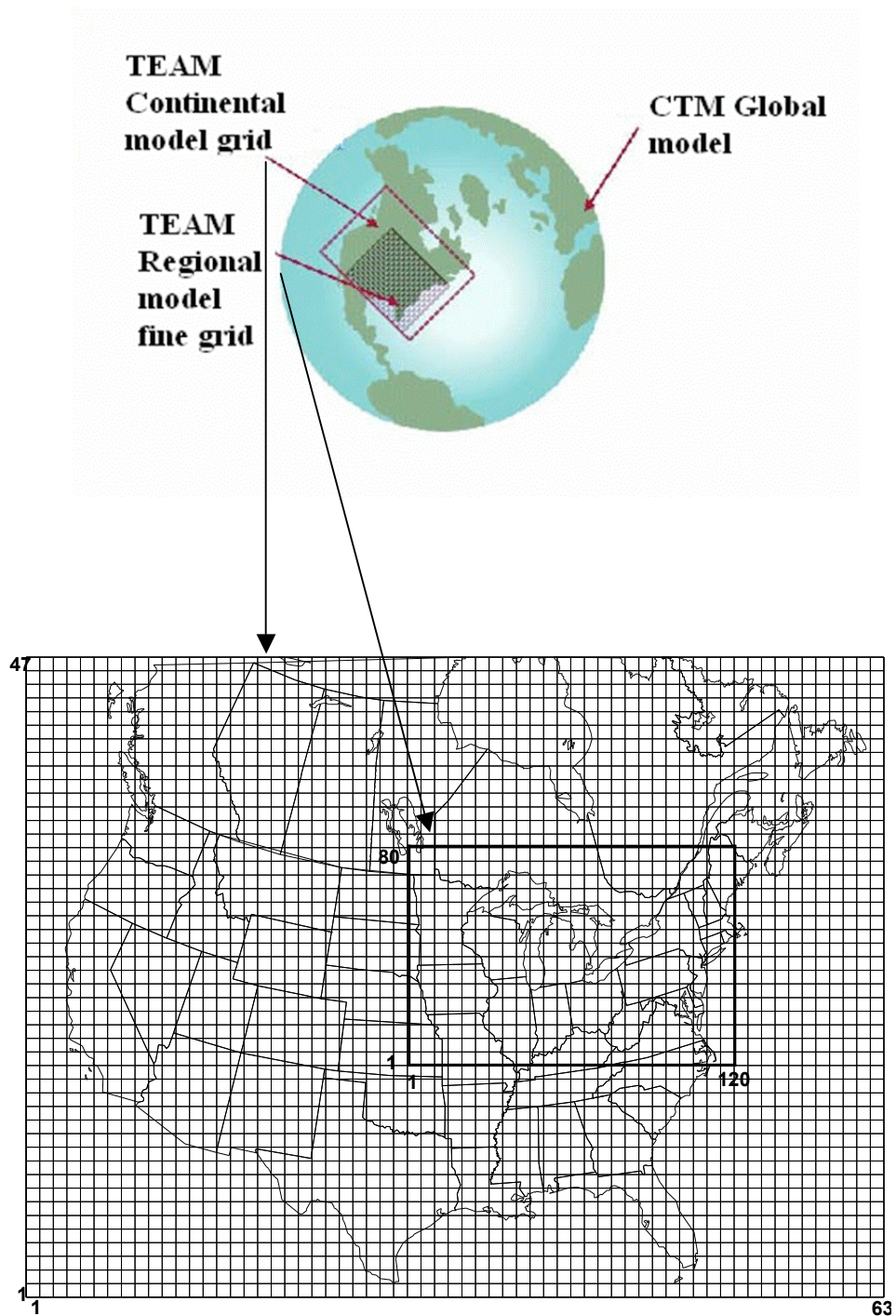


Figure 2. Multi-scale modeling domain with global, continental and regional domains.

The development, evaluation and applications of TEAM have been reported in eight peer-reviewed publications in scientific journals and in numerous technical reports and conference presentations. The development and evaluation of TEAM have been funded by the Electric Power Research Institute (EPRI). Under a project sponsored by the New York State Energy Research and Development Agency (NYSERDA), TEAM was transferred to the New York State Department of Environmental Conservation (NYSDEC). Under a project sponsored by the Wisconsin Department of Natural Resources (WDNR), the mercury chemistry of TEAM was transferred to another air quality model typically used to predict ozone and particulate matter (PM) (Yarwood et al., 2003). TEAM is currently part of the North American Mercury Model Intercomparison Study (NAMMIS) that includes several mercury models developed by the U.S. Environmental Protection Agency (EPA), Environment Canada, Atmospheric & Environmental Research, Harvard University and others.

5. Contribution of Wisconsin Coal-Fired Power Plants to Mercury Deposition

The TEAM emission inventory was adapted for the Wisconsin simulations by using the Wisconsin Department of Natural Resources (DNR) emission inventory for Wisconsin sources other than coal-fired power plants. The Wisconsin DNR emissions differed by less than 1% from the AER/EPRI emission inventory for Wisconsin coal-fired power plants and the AER/EPRI emission inventory was not modified for this source category. The Wisconsin emission inventory is summarized in Table 1.

Figure 3 presents the simulated total (i.e., wet + dry) mercury deposition over the modeling domain for the base simulation using 1998 meteorology as input to the model, with all natural and anthropogenic sources of atmospheric mercury from a 1999/2000 inventory. Figure 4 illustrates the TEAM simulation results for the contribution of Wisconsin coal-fired power plant mercury emissions to mercury deposition. The results were obtained by comparing the base simulation ((i.e., the simulation with all natural and anthropogenic emissions, including power plant emissions, shown in Figure 3) with a simulation conducted with no emissions from Wisconsin coal-fired power plants (i.e., the base emission inventory minus all Wisconsin coal-fired power plant emissions). The results are presented in terms of the relative change in mercury deposition with respect to the base simulation. These results show that mercury emissions from coal-fired power plants located in Wisconsin contribute less than 5% to total mercury deposition over most areas of the state. The northwestern part of the state has less than a 1% contribution to mercury deposition.

The results of this modeling cannot be used to draw conclusions about the local impacts of individual sources, because the simplified treatment of power plant emissions in TEAM is likely to overestimate the local impacts of individual point sources (see discussion in Section 6). As summarized in Table 2, Wisconsin coal-fired power plants contribute from 1 to 4% to atmospheric mercury deposition at the four sites of the Mercury Deposition Network (MDN) in Wisconsin (see Figure 5 for the locations of these sites).

Table 1. 1999/2000 Emission Inventory by Source Category (kg/yr) used in the TEAM simulations for Wisconsin.

Source Type	WDNR Inventory
Coal-fired Power Plants	940 ^(a)
Other Coal Combustion	190
Non-utility Petroleum Product Combustion	233
Wood Burning	5
Municipal Waste Incineration	80
Medical Waste Incineration	273
Pulp & Paper	2
Lamp Breakage	49
Lime Manufacturing	58
Human Cremation	17
Chloralkali	505
Mobile Sources	105
Other Point Sources	155
Other Area Sources	373
Total	2985

(a) AER / EPRI inventory value, Wisconsin DNR value was 947 kg/yr.

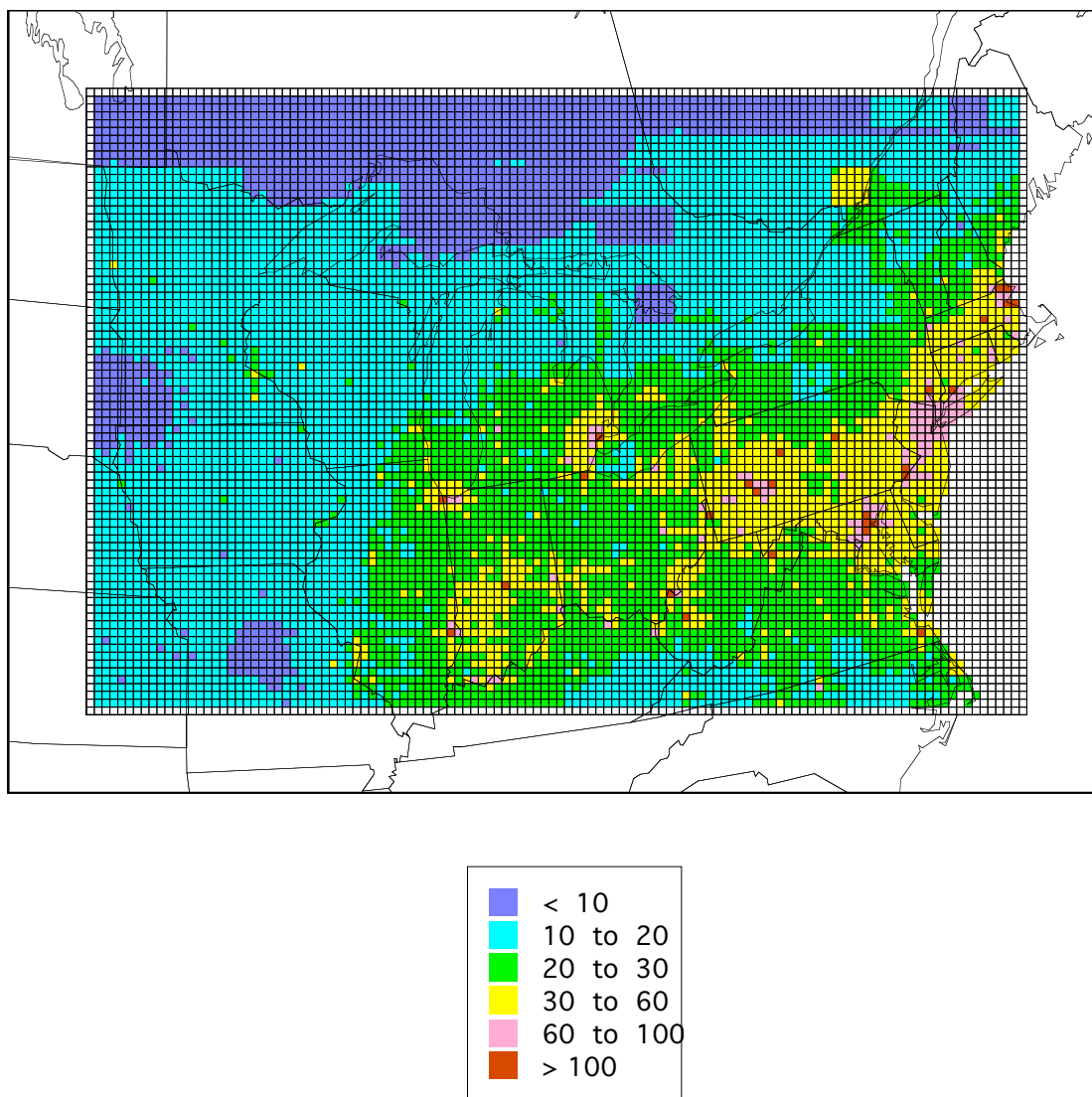


Figure 3. Total deposition flux of mercury ($\mu\text{g}/\text{m}^2\text{-yr}$) simulated with TEAM with all natural and anthropogenic emissions of mercury.

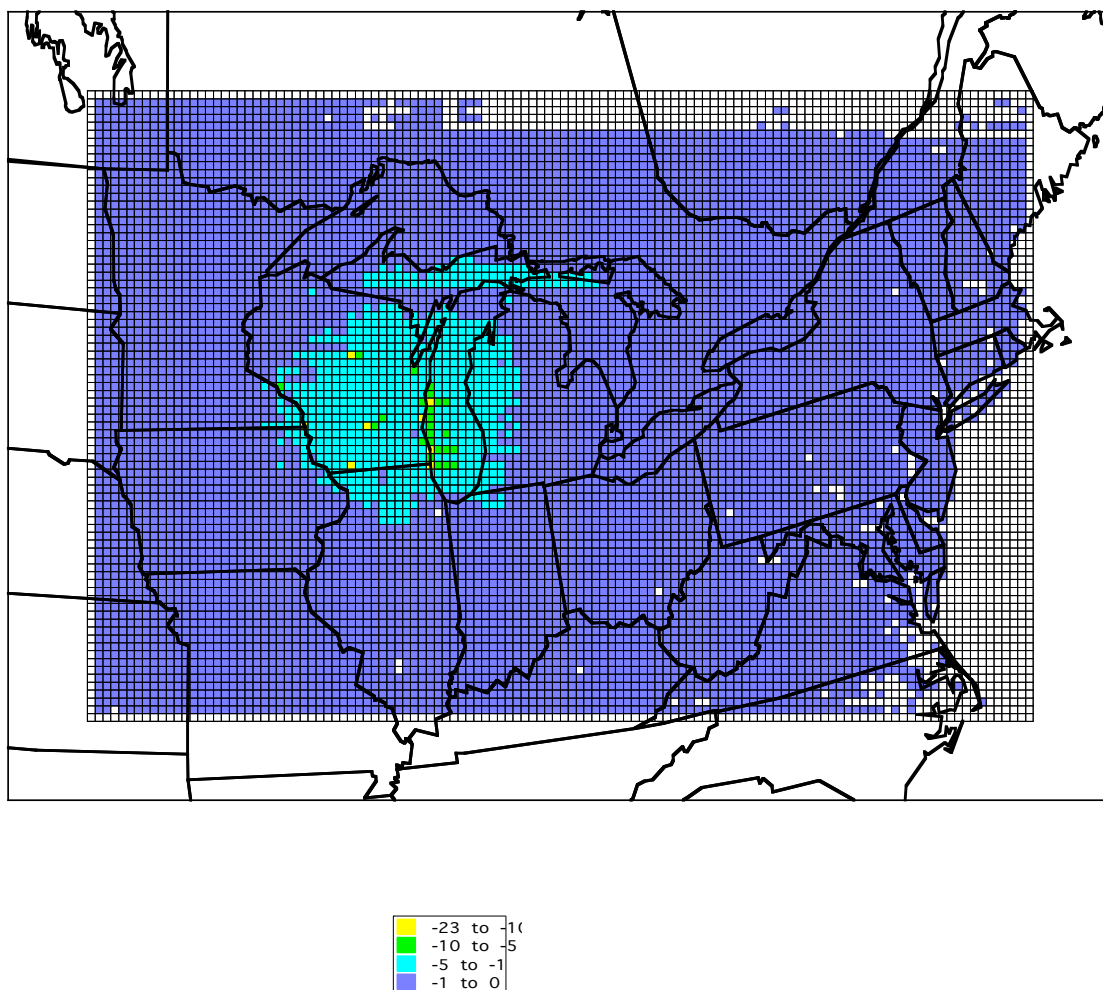


Figure 4. Percent change in the simulated total deposition flux of Hg over the modeling domain with coal-fired power plant mercury emissions in Wisconsin set to zero. (Note that these regional model simulations do not properly characterize local impacts of individual point sources; see Section 6.)

Table 2. Contribution of Wisconsin coal-fired power plant emissions to atmospheric mercury deposition at Wisconsin MDN sites relative to the base simulation.

Wisconsin MDN Site	Relative contribution of Wisconsin coal-fired power plant emissions
WI08	1%
WI09	1%
WI36	1%
WI99	4%

National Atmospheric Deposition Program Mercury Deposition Network

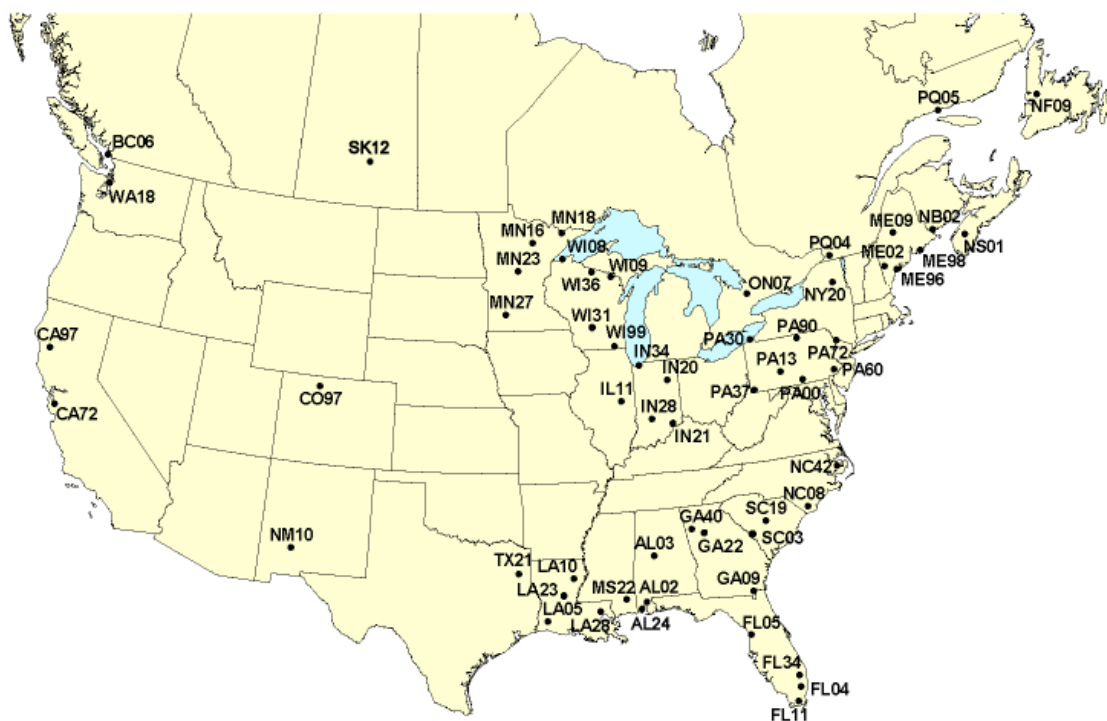


Figure 5. Map of Hg deposition monitoring stations in the Mercury Deposition Network (MDN, 2000) (Note: Sites in Wisconsin operational in 1998 were WI08, WI09, WI36, WI99).

6. Summary of New Relevant Studies

6.1 Atmospheric mercury chemistry

The chemical kinetic mechanism used in TEAM and in the global CTM to simulate the atmospheric chemistry of mercury is continuously updated to reflect the state of the science. However, no major modifications have been made to this mechanism since 2002; the kinetics of the gas-phase oxidation of Hg^0 by Cl_2 was updated but this reaction is not a major pathway for Hg^0 oxidation (See Table A-1 for the current kinetics of the reactions used in TEAM). New laboratory data have become available for the gas-phase kinetics of the oxidation of Hg^0 by ozone. However, this kinetics was challenged on the basis that it did not reflect atmospheric conditions (Calvert and Lindberg, 2005) and it was found to be inconsistent with our current understanding of the global cycling of mercury (Seigneur et al., 2006a); therefore, the kinetics of this reaction was not changed in TEAM and is still the same as that used in the 2002 simulations. New laboratory data have also become available for the gas-phase oxidation of Hg^0 by halogen radicals, primarily Br and BrO. These reactions are important in the Arctic and Antarctic during spring (Ariya et al., 2004) and possibly in the marine boundary layer (Mason and Sheu, 2002) and upper atmosphere (Holmes et al., 2006). However, these reactions are not expected to have a significant effect in the continental United States, except perhaps in marine coastal areas, and, consequently, the TEAM chemical kinetic mechanism has not been updated to take these reactions into account. Finally, the possible reduction of Hg^{II} in power plants, which is discussed below, is an area of current research; no specific reaction has yet been identified in the laboratory and this possible chemical pathway is not included in the TEAM chemical mechanism.

6.2 Evaluation of the contribution of coal-fired power plant emissions to mercury deposition

Model performance evaluation is typically conducted to evaluate the ability of a CTM to reproduce ambient concentrations and deposition fluxes of the chemical species of interest. It is also of interest to evaluate whether a CTM is able to reproduce the contribution of an emission source category to ambient concentrations or deposition fluxes. Such an evaluation is summarized here with data from the Steubenville study where the contribution of the coal combustion source category to mercury wet deposition was estimated using receptor modeling techniques. Because TEAM was used here to investigate the relative effects of Wisconsin coal-fired power plant emissions on atmospheric mercury deposition, it is of particular interest to compare the TEAM predictions at the Steubenville site with the results of the receptor modeling analyses.

Measurements of mercury wet deposition conducted at Steubenville, Ohio, have been analyzed using receptor modeling techniques (Positive Matrix Factorization, PMF, and UNMIX) to identify the contributions of major source categories (Keeler, 2006; Keeler et al., 2006). The receptor modeling results indicate a contribution of about 70% (with an estimated uncertainty of 15%; i.e., a range of 55 to 85%) for the emissions due to coal combustion (i.e., including but not limited to coal-fired power plants). (The uncertainty in the receptor analysis may actually be greater than 15% because of several

simplifying assumptions such as back-trajectories limited to three days; note also that the term “local” used by Keeler et al. actually refers to a regional scale in terms of air quality modeling.)

The contribution of coal-fired power plant emissions to mercury deposition at Steubenville was estimated with TEAM by conducting a simulation with no mercury emissions from all U.S. coal-fired power plants and comparing the mercury deposition fluxes with those obtained in a base simulation. In the model grid cell where Steubenville is located, TEAM predicts that 62% of the mercury wet deposition is due to U.S. coal-fired power plant emissions. This estimate is well within the range of 55 to 85% obtained with the receptor modeling techniques. Therefore, the results of Keeler et al. (2006) corroborate the TEAM simulation results and provide credibility for the use of TEAM to estimate the effect of coal-fired power plant emissions to mercury deposition within the United States.

6.3 Contribution of natural and non-U.S. anthropogenic sources to mercury deposition in Wisconsin

AER used the global/continental/regional modeling system (see Figure 2) to calculate the contribution of sources outside North America to mercury deposition in the United States, with 20 km resolution over Wisconsin. Figure 6 presents the results of these simulations. Model simulation results show that all natural sources and anthropogenic sources outside North America contribute about 60 to 75% of mercury deposition over Wisconsin (i.e., North American anthropogenic sources contribute 25 to 40%). At Brule River in northern Wisconsin, natural and anthropogenic sources outside North America were calculated to contribute 74% (i.e., anthropogenic North American sources contributed 26%); at Devil’s Lake in southern Wisconsin, they contributed 68% (i.e., anthropogenic North American sources contributed 32%).

Selin et al. (2007) of Harvard University applied the global CTM GEOS-Chem to estimate the contribution of North American sources to mercury deposition in the United States. The GEOS-Chem simulation result, shown in Figure 7, indicate that less than 20% of mercury deposition in Wisconsin is due to North American sources.

EPA used a combination of GEOS-Chem and the continental Community Multi-scale Air Quality model (CMAQ) to estimate the contribution of sources outside North America to mercury deposition in the United States with a finer resolution than allowed by GEOS-Chem (about 200 km resolution with GEOS-Chem versus 36 km resolution with CMAQ). The simulation results are presented in Figure 8 (Figure 11.1 in CAMR Technical Support Document: EPA, 2005a). According to EPA’s analysis, natural and anthropogenic sources of mercury outside North America are estimated to contribute more than 85% of mercury deposition in northern Wisconsin (i.e., less than 15% is due to North American sources) and more than 75% over most of southern Wisconsin (i.e., less than 25% is due to North American sources). There is one location on the lakeshore where the global contribution is low, between 15 and 25% (i.e., between 75 and 85% due

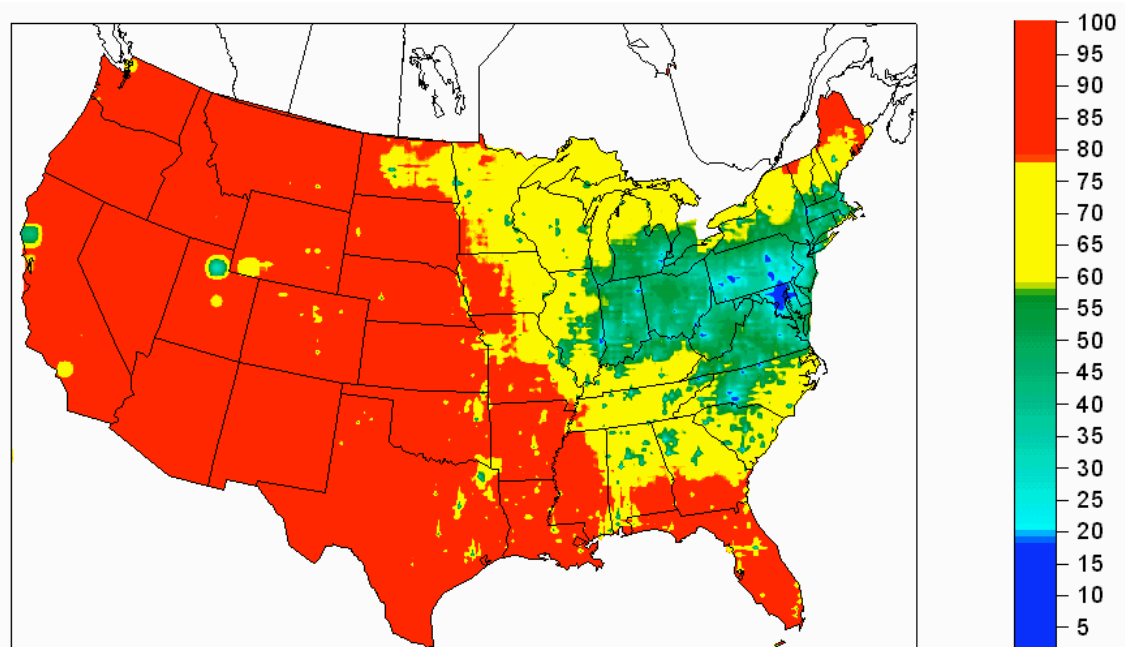


Figure 6. Contribution of sources other than anthropogenic U.S. sources to mercury deposition in the United States. The contribution is mostly above 60% in Wisconsin; i.e., all U.S. anthropogenic sources are estimated to contribute less than 40% to mercury deposition in Wisconsin (Source: adapted from Seigneur et al., 2004).

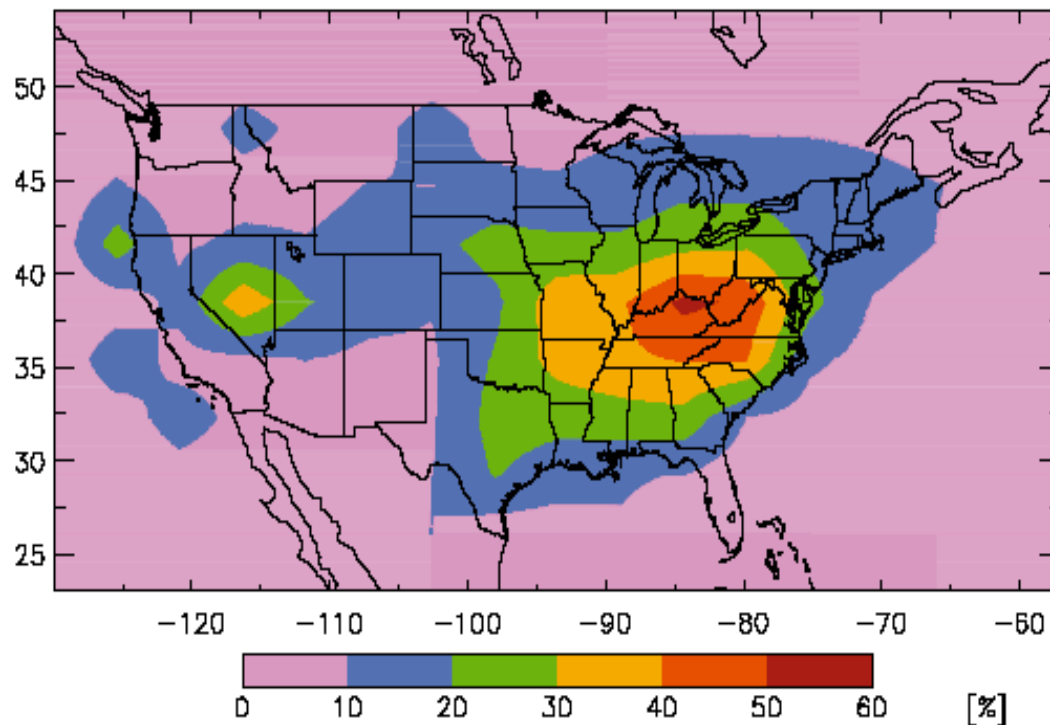


Figure 7. Percentage contribution from North American anthropogenic sources to annual mercury deposition simulated with the GEOS-Chem model for 2003. North America is defined as the geographical domain shown in the figure. The contribution of North American anthropogenic sources to mercury deposition in Wisconsin is simulated to be less than 20%. (Source: Selin et al., 2007.)

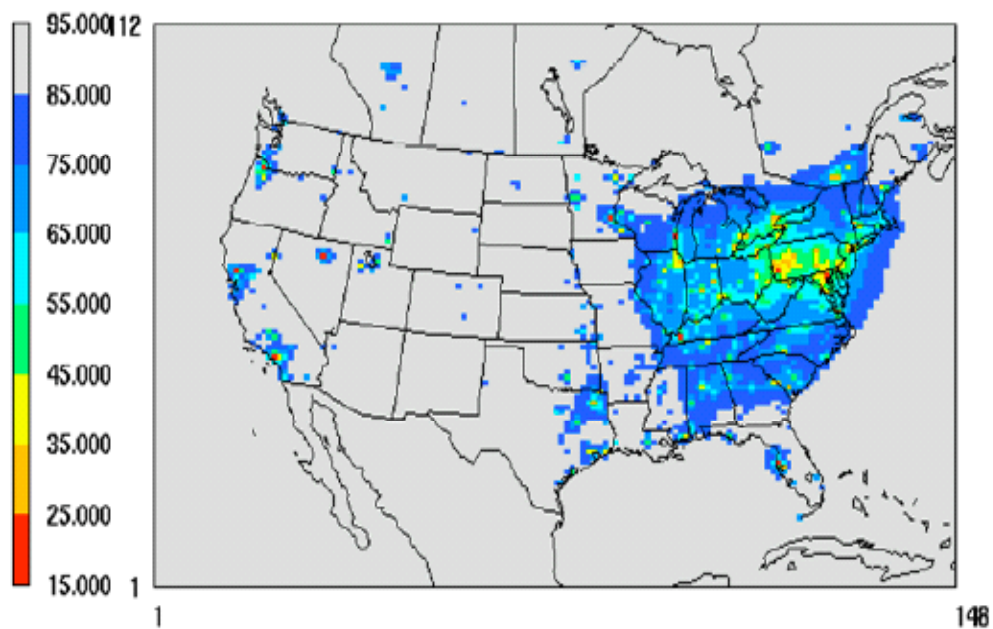


Figure 8. Percent of total mercury deposition attributable to global sources estimated using the GEOS-Chem/CMAQ modeling system for 2001 (Source: Figure 11.1 in CAMR Technical Support Document: EPA, 2005a).

to North American sources). As discussed below, grid-based models tend to overestimate local mercury deposition in the vicinity of elevated point sources and this North American contribution may, therefore, be an overestimate.

Differences between these three modeling studies result from differences in the model formulations, inputs (meteorology, emissions), and spatial resolution. In any case, all studies show the large contribution of sources outside North America to mercury deposition in Wisconsin.

6.4 EPA CMAQ model simulations in support of CAMR

EPA used CMAQ to simulate the atmospheric deposition of mercury in support of the Clean Air Mercury Rule (CAMR). As part of this work, they conducted a base simulation for 2001 and a simulation with no mercury emissions from U.S. coal-fired power plants (everything else remaining unchanged). Comparing these two simulations provides quantitative estimates of the contribution of coal-fired power plants to mercury deposition in the United States. Figure 9 presents those results.

It appears that U.S. coal-fired power plants contribute less than $2 \mu\text{g}/\text{m}^2\text{-yr}$ to total mercury deposition in most of Wisconsin. Some limited areas in southern Wisconsin show contributions in the range of 2 to $8 \mu\text{g}/\text{m}^2\text{-yr}$. On average, all U.S. coal-fired power plants are calculated to contribute currently only 8.4% of total mercury deposition in Wisconsin (EPA, 2006). This result is consistent with the results of the TEAM simulation presented above.

6.5 EPA REMSAD model simulations

EPA conducted simulations with the Regional Modeling System for Aerosols and Deposition (REMSAD) to estimate the contribution of all anthropogenic mercury emissions from individual states to mercury deposition in the United States (EPA, 2003). The REMSAD simulation suggests that less than 5% of mercury emitted from all anthropogenic Wisconsin sources is deposited within Wisconsin; i.e., more than 95% of mercury emitted in Wisconsin is transported outside of Wisconsin. This result exemplifies the fact that the great majority of emissions from Wisconsin sources is not deposited within Wisconsin.

6.6 Local deposition of mercury from stacks

It was mentioned in Section 5 that the TEAM simulation results are likely to overestimate mercury deposition in the vicinity of Wisconsin coal-fired power plants. This statement is based on recent work where TEAM mercury deposition results were compared to mercury deposition results from a plume model (Seigneur et al., 2006b). Compared to a plume dispersion model, which is typically used to estimate maximum contributions of pollutants to local areas, the grid-based model TEAM overestimated mercury deposition in the proximity of large elevated point sources such as power plant stacks over an area commensurate with the resolution of the grid-based model. This

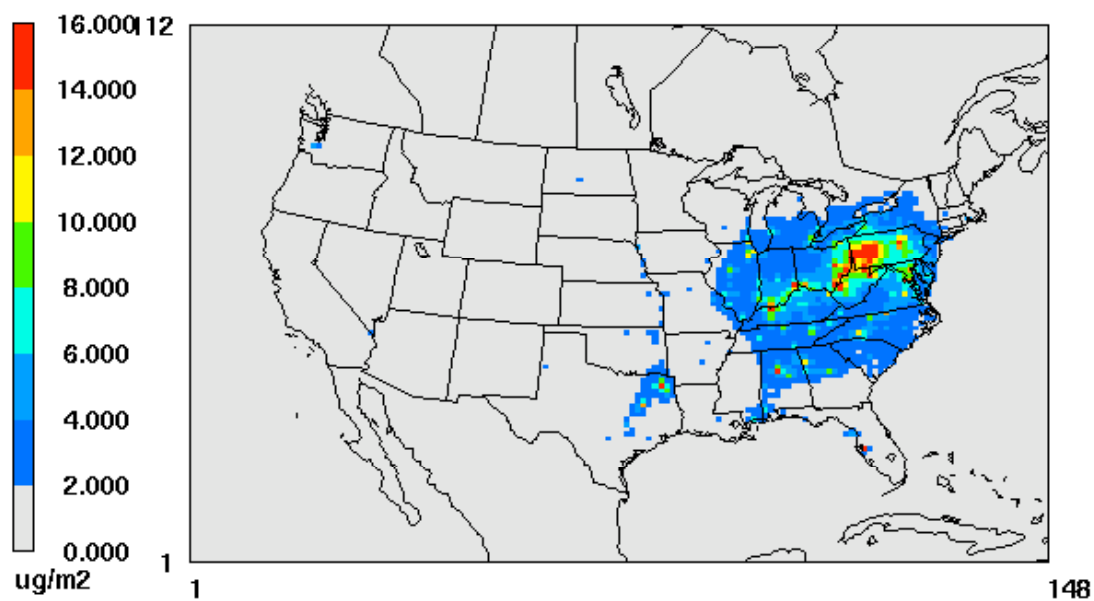


Figure 9. Decrease in mercury deposition due to 100% reduction (zero-out) in mercury emissions from all U.S. coal-fired power plants simulated with the CMAQ model for 2001 (Source: Figure 4 in EPA CAMR Technical Support Document, 2005b).

overestimation is up to a factor of two and is due to the fact that grid-based models tend to overestimate the vertical mixing of plumes, thus artificially enhancing dispersion to the Earth's surface and hence the dry deposition. Therefore, the highest contributions of Wisconsin coal-fired power plants to mercury deposition shown in Figure 4 (yellow grid squares), which occur in the vicinity of those power plants, are likely to be overestimates.

6.7 Evidence for reduction of divalent mercury (RGM) in power plant plumes

Mercury emissions from various sources are a combination of the different speciated forms of mercury, namely, Hg^0 , Hg^{II} and Hg_p . Several recent experimental studies provide direct and circumstantial evidence of a change in mercury speciation in power plant plumes between the stack and downwind locations that corresponds to a decrease in Hg^{II} and a corresponding increase in Hg^0 . This change in mercury speciation could be due to uncertainties in the speciation reported in the stack emission measurements or to a currently unknown chemical reaction taking place in the plume. It may significantly affect deposition predictions downwind of power plants with a high fraction of Hg^{II} emissions. We summarize some of the relevant studies below.

Ambient sampling of Hg species (Hg^{II} , Hg^0 , and Hg_p), NO_y (NO_y represents reactive odd nitrogen compounds, including NO, NO_2 , HNO_3 and organic nitrogen oxides) and SO_2 was conducted with continuous monitors downwind of coal-fired power plants in the Atlanta region (Edgerton et al., 2006). The SO_2/NO_y ratio was used as a signature of individual power plants assuming that there is little oxidation and deposition of SO_2 and NO_y between the stacks and the sampling site (several miles downwind). Then, the corresponding speciated mercury measurements from the monitoring locations were compared with the estimated mercury speciated emissions for the power plants based on emission data collected during the Information Collection Request (ICR) program. The results from that study suggest that the $\text{Hg}^{\text{II}}/\text{Hg}^0$ ratio downwind from those power plants is lower than the $\text{Hg}^{\text{II}}/\text{Hg}^0$ ratio estimated from the ICR data for the stack emissions while total mass of Hg does not vary significantly between the two locations. An average 14% reduction per hour of Hg^{II} to Hg^0 was observed across different seasons, various power plants and different plume travel times ranging up to 15 hours depending on the source and meteorological conditions.

Modeling of the fate and transport of mercury in nine of the power plant plume events analyzed by Edgerton et al. (2006) was conducted by Lohman et al. (2006) to investigate the possible reasons for this change in mercury speciation between the stacks and the downwind sampling site of Yorkville, GA. Lohman et al. (2006) ruled out the possibility of Hg^{II} dry deposition because (1) insufficient Hg^{II} deposition took place between the stack and the sampling site (the plumes remained aloft during part of the travel time) and (2) the mercury/ SO_2 mass balance was not conserved if a greater dry deposition rate was assumed and used in the plume model. Lohman et al. (2006) proposed three hypotheses to explain the phenomenon: (1) a reaction converting Hg^{II} to Hg^0 took place in the power plant plumes, (2) the speciation of the stack emissions was incorrect (different sampling methods are used for stack sampling – Ontario Hydro method – and ambient sampling – Tekran instruments), or (3) a fast reduction reaction

took place after Hg^{II} deposited to the ground along the plume trajectory with rapid emission of the resulting Hg^0 .

Some empirical evidence of reduction of Hg^{II} to Hg^0 in coal-fired power plant plumes has also been reported in experiments where the exhaust flue gases from a coal-fired power plant stack were sampled, diluted and analyzed in a Teflon-lined dispersion chamber, and in aircraft measurement campaigns performed in the plumes of the Bowen power plant in Georgia and the Pleasant Prairie power plant in Wisconsin (EPRI, 2006).

Finally, the mercury wet deposition data of the Mercury Deposition Network (MDN) along a west-to-east transect from Minnesota to Pennsylvania show no significant spatial gradient in mercury annual wet deposition fluxes in spite of the fact that the Ohio Valley includes several large mercury emission sources located, under prevailing wind conditions, upwind of Pennsylvania. This result is in sharp contrast with sulfate wet deposition data which show a clear west-to-east gradient (Seigneur, 2005; Vijayaraghavan et al., 2007). Hypotheses for the lack of a west-to-east gradient in mercury wet deposition include: (1) a significant contribution from dry deposition in Pennsylvania, (2) an underestimation of mercury emissions in the upper Midwest, and (3) atmospheric transformation of Hg^{II} to Hg^0 , thereby reducing mercury wet deposition in the region (recall that Hg^0 has an atmospheric lifetime of a few months) (Seigneur et al., 2003a). As a matter of fact, TEAM simulation performance for wet deposition improves when the speciation of the mercury emissions in the source region upwind from and including the Pennsylvania region is modified to reflect the third hypothesis, i.e., using lower Hg^{II} fraction in coal-fired power plant emissions (Seigneur et al., 2003b).

6.8 Mercury speciation in the upper atmosphere

It should also be noted that there is increasing evidence of a global pool of Hg^{II} and Hg_p in the free upper troposphere and lower stratosphere, regions in the atmosphere that range between about 10 and 15 km in altitude (Murphy et al., 2006; Holmes et al., 2006). Such Hg^{II} and Hg_p are produced by the oxidation of Hg^0 at a global scale and their concentrations near the tropopause (about 12 to 15 km in altitude) exceed the Hg^0 concentrations. Large convective storms may extend to altitudes that reach into the upper troposphere (i.e., 10 to 12 km altitude) and may, therefore, lead to precipitation of some of this global background Hg^{II} and Hg_p . Such processes are not currently simulated in regional models of atmospheric mercury; however, including those processes in mercury deposition models would increase the contribution of the mercury global pool to mercury wet deposition and would decrease the contribution of local and regional emissions.

7. Summary

Modeling of the contribution of Wisconsin coal-fired power plants to atmospheric deposition of mercury in Wisconsin was conducted in 2002 using the chemical transport model TEAM. Conclusions were that Wisconsin coal-fired power plants contributed from 1 to 4% to mercury deposition at the four Wisconsin sites of the Mercury Deposition Network and contributed less than 5% in most areas of Wisconsin. Larger

contributions were estimated in the vicinity of power plants; however, TEAM overestimates mercury deposition near elevated stacks.

The results of this modeling study are still valid. Recent advances in our knowledge of atmospheric mercury processes (e.g., oxidation of mercury by bromine species) do not affect significantly the results of the 2002 study. Furthermore, several studies conducted by AER and other groups bring additional information corroborating the results of the 2002 study.

The statistical analysis of mercury wet deposition measurements collected in Steubenville, Ohio, led to an estimate of the contribution of coal combustion sources to mercury wet deposition at that location which is consistent with the prediction of TEAM for that same location, thereby corroborating the ability of TEAM to simulate the effect of emission reduction scenarios on mercury deposition.

Estimates of the contribution of all natural sources and anthropogenic sources outside of North America to mercury deposition in Wisconsin have been made using different modeling systems. Those estimates range from 60 to 85%, i.e., anthropogenic North American sources are estimated to contribute between 15 and 40% to mercury deposition in Wisconsin. Note that the larger estimates of the North American anthropogenic source contribution are obtained with the AER modeling system (which includes TEAM). Other groups estimate lower contribution from North American sources.

Calculations of mercury deposition were conducted by EPA using the CMAQ and REMSAD chemical transport models. EPA calculated with CMAQ that all U.S. coal-fired power plants contributed on average 8.4% to total mercury deposition in Wisconsin. EPA calculated with REMSAD that less than 5% of mercury emitted from Wisconsin anthropogenic sources is deposited within Wisconsin.

New studies have confirmed that (1) grid-based models such as TEAM, CMAQ and REMSAD overestimate mercury deposition in the vicinity of elevated sources such as power plants, (2) reduction of Hg^{II} to Hg^0 may occur in coal-fired power plant plumes, thereby leading to less local mercury deposition of those estimated Hg^{II} emissions, and (3) large storm systems may lead to contribution to wet deposition of mercury from the upper atmosphere, which is not currently taken into account in existing models. These results suggest that the TEAM results are likely to overestimate the contribution of coal-fired power plants to mercury deposition in the vicinity of those plants.

In summary, the results of the 2002 study of mercury deposition in Wisconsin are still valid and studies conducted since 2002 either corroborate or further validate those results.

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Appendix A. Mercury Chemistry in TEAM

Table A-1. Equilibria and reactions of atmospheric mercury used in the TEAM simulations (Source: Seigneur et al., 2006a).

Equilibrium Process or Chemical Reaction	Equilibrium or Rate Parameter ^a	Reference ^b
$\text{Hg}(0) (\text{g}) \rightleftharpoons \text{Hg}(0) (\text{aq})$	0.11 M atm^{-1}	Sanemasa, 1975; Clever et al., 1985
$\text{HgCl}_2 (\text{g}) \rightleftharpoons \text{HgCl}_2 (\text{aq})$	$1.4 \times 10^6 \text{ M atm}^{-1}$	Lindqvist and Rodhe, 1985
$\text{Hg}(\text{OH})_2 (\text{g}) \rightleftharpoons \text{Hg}(\text{OH})_2 (\text{aq})$	$1.2 \times 10^4 \text{ M atm}^{-1}$	Lindqvist and Rodhe, 1985
$\text{HgCl}_2 (\text{aq}) \rightleftharpoons \text{Hg}^{2+} + 2 \text{Cl}^-$	10^{-14} M^2	Sillen and Martell, 1964
$\text{Hg}(\text{OH})_2 (\text{aq}) \rightleftharpoons \text{Hg}^{2+} + 2 \text{OH}^-$	10^{-22} M^2	Sillen and Martell, 1964
$\text{Hg}^{2+} + \text{SO}_3^{2-} \rightleftharpoons \text{HgSO}_3$	$2.1 \times 10^{13} \text{ M}^{-1}$	van Loon et al., 2001
$\text{HgSO}_3 + \text{SO}_3^{2-} \rightleftharpoons \text{Hg}(\text{SO}_3)_2^{2-}$	$1.0 \times 10^{10} \text{ M}^{-1}$	van Loon et al., 2001
$\text{Hg}(\text{II}) (\text{aq}) \rightleftharpoons \text{Hg}(\text{II}) (\text{p})$	34 l/g	Seigneur et al., 1998
$\text{Hg}(0) (\text{g}) + \text{O}_3 (\text{g}) \longrightarrow \text{Hg}(\text{II}) (\text{g})$	$3 \times 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall, 1995
$\text{Hg}(0) (\text{g}) + \text{HCl} (\text{g}) \longrightarrow \text{HgCl}_2 (\text{g})$	$10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall and Bloom, 1993
$\text{Hg}(0) (\text{g}) + \text{H}_2\text{O}_2 (\text{g}) \longrightarrow \text{Hg}(\text{OH})_2 (\text{g})$	$8.5 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Tokos et al., 1998
$\text{Hg}(0) (\text{g}) + \text{Cl}_2 (\text{g}) \longrightarrow \text{HgCl}_2 (\text{g})$	$2.6 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya et al., 2002
$\text{Hg}(0) (\text{g}) + \text{OH} (\text{g}) \longrightarrow \text{Hg}(\text{OH})_2 (\text{g})$	$8.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Sommar et al., 2001
$\text{Hg}(0) (\text{aq}) + \text{O}_3 (\text{aq}) \longrightarrow \text{Hg}^{2+}$	$4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Munthe, 1992
$\text{Hg}(0) (\text{aq}) + \text{OH} (\text{aq}) \longrightarrow \text{Hg}^{2+}$	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1997
$\text{HgSO}_3 (\text{aq}) \longrightarrow \text{Hg}(0) (\text{aq})$	0.0106 s^{-1}	van Loon et al., 2000
$\text{Hg}(\text{II}) (\text{aq}) + \text{HO}_2 (\text{aq}) \longrightarrow \text{Hg}(0) (\text{aq})$	$1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Pehkonen and Lin, 1998 ^c
$\text{Hg}(0) (\text{aq}) + \text{HOCl} (\text{aq}) \longrightarrow \text{Hg}^{2+}$	$2.09 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1998
$\text{Hg}(0) (\text{aq}) + \text{OCl}^- \longrightarrow \text{Hg}^{2+}$	$1.99 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1998

Hg(II) refers to divalent Hg species

^a The parameters are for temperatures in the range of 20 to 25°C, see references for exact temperature; temperature dependence information is available for the Henry's law parameter of Hg(0) and for the kinetic rate parameter of the HgSO₃ reaction.

^b See Seigneur et al., 2006a for references.

^c This reaction has been challenged by Gardfeldt and Johnson, 2003; however, an alternative has not been proposed.